

[illegible]

INVENTORS: Mark Alperovich
Irene Zuhl
Eugene Levich
Arie Chaikin

BLANK ROME COMISKY & McCAULEY LLP
Wigman, Cohen, Leitner & Myers IP Group
900 17th Street, N.W., Suite 1000
Washington, D.C. 20006
(202) 530-7400 (telephone)
(202) 463-6915 (facsimile)

Docket No. 109289.00121

Method of Increasing Fluorescent Signal of Optical Discs with Fluorescent Reading

Field of the Invention

5 The present Invention is in the field of materials for optical memory carriers with high optical memory density and reading by means of fluorescence, such as CD ROM and WORM discs, and three-dimensional optical memory systems.

Background of the Invention

At present, digital data carriers with optical recording, storage and reading experience fast spreading. Usually, the data is recorded by local alteration of optical thickness or the active media reflection ratio, while reading takes place by phase or amplitude changes of the laser beam in the recorded spots.

The most cheap and absolute optical carriers are CD ROM and WORM discs. However, the capacity and signal/noise ratio of the existing optical discs is not enough high for the developed computers and videosystems of the new generation. Thus, there are intensive development of advanced optical memory systems with increased record density, high signal/noise ratio, increased storage and usage stability and low cost. The promising ways of increasing optical carrier capacity are:

- 20 • increased number active bits per active layer due to reduced pit length and increased number of pits;
- multilayer disc creation.

These ways were realized in the recently launched DVD standard, where pits are half in size, and number of layers reaches 4 - two from each side of the substrate. It allows reaching 20 GB capacity on disc.

At the same time, future increase of active layers on disc with reading by means of reflection causes rapid rise in the system price and lowers the quality of recorded data reproduction. Thus, future increase of disc capacity is not possible. The patents JP 63,195,838 (12.08.1988); JP 02,308,439 (21.12.1990) describe reading by means of fluorescence. The principle idea is that after recording the recorded spots are non-fluorescent, and the background is fluorescent. At reading, the relevant laser beam excites fluorescent light, which is registered on the detector.

The above patents describe single-layer optical discs with laser recording, i.e. of WORM type.

At the same time, the main advantage of fluorescent reading is in its most suitability for three-dimensional optical memory carriers, such as a multilayer disc [B. Glushko, V. Krupkin, E. Levich]

The principle construction of a multilayer optical disc with fluorescent reading is described in [B. Glushko, US Provisional Patent Application 8/05/97, N 25457].

Single-layer optical discs, where data is recorded in pit or spiral grooves, filled with fluorescent material, are laminated on each other to form a multilayer system, where active layers containing fluorescent pits or grooves with 0.5-1.0 mkm depth are separated by inactive intermediate layers of 20-50 mkm depth, transparent for the excitation laser wavelength and fluorescent light. Fluorescent media for a multilayer optical disc with fluorescent reading shall meet a range of requirements, the most important being:

1. Fluorescent media absorption range shall coincide with the reading laser wavelength.
2. Quantum yield of fluorescent media shall be the highest possible and shall stay the same during long-term storage and use.
3. Absorption and fluorescence ranges shall not overlap significantly not to cause repeated absorption of fluorescent light.
4. Fluorescent composition shall not disperse the passing excitation radiation and fluorescent light.
5. Fluorescent light shall also coincide well with the matrix and shall not migrate from it.
6. Fluorescent composition shall fill the pits or groove well and shall not tincture the space in between.
7. The solution used for filling pits or grooves shall not solve the substrate, carrying pits or grooves, or change their geometry and size.
8. Refraction ratio of the fluorescent composition shall be close to the one of the substrate, carrying pits or groove.
9. Characteristics of the fluorescent composition shall not be effected by storage or use of a multilayer optical disc.

All these requirements make it a non-trivial task to solve. It is especially difficult to achieve high intensity of fluorescence from the active layer, as if we consider it to be 100-500 nm thick, the concentration of fluorescent dye shall be equal to $3-20 \times 10^{-2}$ Mol per kg of polymer. At such concentration, the intensity of fluorescence from most of the organic luminophores will be rapidly reduced or can disappear at all due to the formation of associated forms of the dye

with sandwich structure in the polymer. Such forms are non-fluorescent and they extinguish fluorescence of monomeric forms of the dye. Ability of the dye to form dimmers and other associates is much connected to the composition and structure of the polymeric matrix, used plasticizers and other ingredients of the polymeric composition. However, such high concentrations of the dye ($3-20 \times 10^{-2}$ Mol/kg) nearly always cause formation of associates.

Recently the medias for high-density optical CD ROM and WORM discs with fluorescent reading, including multilayer discs, were described in [M. Alperovich, E. Levich, I. Zuhl, et al. US Provisional Patent Appl. N Fluorescent Composition for production of the optical memory discs of CD ROM type; M. Alperovich, E. Levich, I. Zuhl, et al. US Provisional Patent Appln. Organic dye-in-polymer (DIP) medium for WORM disks with fluorescent reading; M. Alperovich, E. Levich, I. Zuhl, et al. US Provisional Patent Appln. Optical recording medium for fluorescent WORM discs; M. Alperovich, E. Levich, I. Zuhl, et al. US Provisional Patent Appln. Optical recording medium for fluorescent WORM disk including penetrated ion pairs in organic dyes].

The proposed fluorescent compositions were used for production of CD ROM and WORM discs with fluorescent reading, including multilayer structures. The recorded digital data was read on special drives, providing registration of the fluorescent signal. At the same time, future increase of fluorescence intensity from active layers of the optical discs is needed to increase stability and quality of the read data, to simplify the construction and to lower cost of production of the reading devices for fluorescent discs. This will also allow increasing the number of active layers on multilayer discs, thus increasing the optical memory capacity.

Summary of the Invention

Taking the above into consideration, the purpose of this Invention is the development of method of increasing fluorescent signal level from the optical discs with fluorescent reading to obtain optical memory with high capacity.

The other purpose of the present Invention is the development of method of increasing fluorescent signal level from the optical discs with fluorescent reading to receive higher stability and reproduction quality, simplify the construction and to lower cost of the device for reading fluorescent signal from optical discs.

The future purpose of this Invention is the development of method of increasing fluorescent signal level from the optical discs with fluorescent reading both for single-layer and multilayer optical memory materials with high capacity and high contrast.

According to the purpose of the present Invention, the above method of increasing the fluorescent signal from optical discs with fluorescent reading assumes use in the fluorescent composition of high-molecular compounds, plasticizers and other ingredients, preventing formation of non-fluorescent dimmers and other dyes associates in the active media.

According to the other purpose of the present Invention, the above method of increasing the fluorescent signal from optical discs assumes use of a primer between the substrate and the active layer to preserve the pits or grooves on the substrate from aggressive effect of solvents, containing the fluorescent composition.

According to the future purpose of the constant Invention, the above method of increasing the fluorescent signal from optical discs assumes using in the polymer compositions of active layers the adds, improving adhesion of the active layers to the substrate or the primer.

According to the further purpose of the present Invention, the above method of increasing the fluorescent signal from optical discs assumes using in the substrate or primer the substances, providing effective absorption of non-fluorescent dimmers and other associates of the ionic pairs of cationic dyes in the active layer on the boundary between the substrate or the primer with active layer.

Detailed Description of the Preferred Embodiments

Below is the detailed description of the most preferred embodiments of the purposes of the present Invention.

First, we shall consider the variant, when the substrate - a transparent disc from polycarbonate (PC) or polymethyl methacrylate (PMMA) with pits or grooves 0.1-0.5 $\mu\mu$ deep - is covered with a primer, which is later covered with an active layer, containing at least a fluorescent dye, film-making polymer, plasticizers and other ingredients, preventing formation of non-fluorescent dimmers and other associates of the dye, thus providing high fluorescence of the dye.

The primer is produced using different materials, providing high adhesion to polycarbonate and polymethyl methacrylate substrates, evenly distributed upon the substrate, pits

and grooves surface, forming a film 10-100 nm thick, impermeable for the solvents and other ingredients of the active layer.

Good adhesion of the active layer to the primer shall also be provided. The materials, forming the primer, can be: liquid silica glass, Colcoat N-103X product by Colcoat Co., Ltd. (Japan), polyvinyl alcohol, heat treated after depositing on the substrate, thermosetting resins, including epoxy, phenol-, urea- and melamine-formaldehyde resins, polyorganosiloxanes, as well as latexes – divinyl styrene, divinylonitrile, styrene acrylate, alkyd, acrylate, etc. The fluorescent dye of the active layer with maximum absorption near the recording laser wavelength is chosen among the xanthene dyes of the eosine and rhodamine groups, acridine, oxazine, azine, perylene, violanthrole, cyanine, phthalocyanine dyes, indigoid colors and porphyrines.

The content of fluorescent dye in the layer is 0.1-10%.

Film-forming polymer can be chosen among a wide range of resins, for example: cellulose esters, such as nitrocellulose, cellulose acetate, cellulose acetate butyrate; cellulose ethers such as methyl cellulose, ethyl cellulose, butyl cellulose; vinyl resins such as polyvinyl acetate, polyvinyl butyral, polyvinyl acetal, polyvinyl alcohol and polyvinyl pyrrolidon; acrylic resins such as polymethylmethacrylate, polybutyl acrylate, polymethacrylic acid, polyacrylic amid and polyacrylonitrile, polyvinylchloride, perchlorvinyl resin.

Film-forming properties of the used resins and the plasticity of the recording layer can be improved by adding to resins the proper plactisizer, such as dibutyl phthalate, dioctyl phthalate or tricresyl phosphate.

To create a recording layer of the present Invention, the above-mentioned ingredients are dissolved in organic solvent or introduced in it as microcapsules less than 0,2 mkm in size, prepared by known methods, with future covering the substrate with this compound by spin coating, roller coating or dip coating.

The organic solvent is usually selected from alcohols, ketones, amides, sulfoxides, ethers, esters, halogenated aliphatic hydrocarbons or aromatic solvents. Examples of such solvents include methanol, ethanol, iso-propanol, iso-butanol, tetrafluoro-ethanol, diacetone alcohol, methyl cellosolve, ethyl cellosolve, acetone, methylethylketone, cyclohexanone, N,N-dimethhylformamide, N,N-dimethylacetamide, dimethylsulfoxide, tetrahydrofurane, dioxane, ethyl acetate, chloroform, methylene chloride, dichloroethane, toluene, xylene or their mixtures.

Various surface-active substances, such as butyl glycol, propylene glycol, dimethyl glycol, diethyl glycol, etc., improve adhesion of the active layers to the substrate or the primer, as well as heat the material at 100-120°C.

The other variant of realizing the purposes of the present Invention differs from the previous one by that the substrate is formed by a polymer, providing effective absorption of non-fluorescent dimmers and other associates of the ionic pairs of cationic dyes on its boundary with the active layer, thus providing good adhesion of the active layer to the substrate. The substrate is covered with the active layer, containing a fluorescent dye, soluble in hydroxyl solvents of the film-forming polymer, a plasticizer and the add, which improves adhesion of the active layer to the substrate.

Polyvinylchloride (PVC) and its co-polymers form the substrate.

The below examples illustrate this Invention, thus not limiting it.

Example 1.

The solution of 1% polyvinylacetate (PVA), 0.013% 3-Diethylamino-7-diethylaminophenoxazonium perchlorate (Ox-1) and 0.2% dioctylphthalate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 2.

The solution of 1% polyvinylacetate (PVA), 0.039% 3-Diethylamino-7-diethylaminophenoxazonium perchlorate (Ox-1) and 0.2% dioctylphthalate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 3.

The solution of 1% polyvinylacetate (PVA), 0.078% 3-Diethylamino-7-diethylaminophenoxazonium perchlorate (Ox-1) and 0.2% dioctylphthalate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 4.

The solution of 1% nitrocellulose (NC), 0.013% 3-Diethylamino-7-diethylaminophenoxazonium perchlorate (Ox-1) and 0.2% dioctylphthalate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 5.

The solution of 1% nitrocellulose (NC), 0.039% 3-Diethylamino-7-diethylaminophenoxazonium perchlorate (Ox-1) and 0.2% dioctylphthalate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 6.

The solution of 1% nitrocellulose (NC), 0.078% 3-Diethylamino-7-diethylaminophenoxazonium perchlorate (Ox-1) and 0.2% dioctylphthalate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 7.

The solution of 1% polyvinylacetate (PVA), 0.013% 1,1', 3,3,3', 3'-Hexamethylindodicarbocyanine iodide (HIDC) and 0.2% dioctylphthalate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 8.

The solution of 1% polyvinylacetate (PVA), 0.039% 1,1', 3,3,3', 3'-Hexamethylindodicarbocyanine iodide (HIDC) and 0.2% dioctylphthalate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 9.

The solution of 1% polyvinylacetate (PVA), 0.078% 1,1', 3,3,3', 3'-Hexamethylindodicarbocyanine iodide (HIDC) and 0.2% dioctylphthalatate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 10.

The solution of 1% nitrocellulose (NC), 0.013% 1,1', 3,3,3', 3'-Hexamethylindodicarbocyanine iodide (HIDC) and 0.2% dioctylphthalatate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 11.

The solution of 1% nitrocellulose (NC), 0.039% 1,1', 3,3,3', 3'-Hexamethylindodicarbocyanine iodide (HIDC) and 0.2% dioctylphthalatate in ethanol and ethyl cellusolve (1:1) was used for preparing the fluorescent composition. The solution was filtered and deposited on the substrate.

Example 12.

The solution of 1% polymethylmetacrilate (PMMA), 0.013% Oxazine 725 Perchlorate (Exciton, Inc.)(Ox-1) and 0.2% dioctylphthalatate in methylenechloride and dioxane (1:4) was used for preparing the fluorescent composition. The solution was filtered, deposited on a polycarbonate disc with a liquid silica glass sub-layer and dried.

Example 13.

The solution of 1% chlorine (PCV), 0.013% Oxazine 725 Perchlorate (Exciton, Inc.)(Ox-1) and 0.2% dioctylphthalatate in methylenechloride and dioxane (1:4) was used for preparing the fluorescent composition. The solution was filtered, deposited on a polycarbonate disc with a liquid silica glass sub-layer and dried.

Effect of increasing of I_{η} at exchanging PVC for NC

Ex. #	Dye concentration Mol/kg	Substrate type	Absorption				Fluorescence	
			D_1	D_2	D_2 / D_1	$\frac{1}{2}$	$\lambda_{\text{flour.}} \text{ (nm)}$	I_{η}
1.	OX1+PVA	PC	0.034	0.014	0.41	14.3	668	0.530
2.	OX1+PVA	PC	0.078	0.040	0.51	15.1	668	0.367
3.	OX1+PVA	PC	0.161	0.103	0.64	18.1	671	0.318
4.	OX1+NC	PC	0.057	0.021	0.37	15.0	675	0.991
5.	OX1+NC	PC	0.122	0.048	0.39	13.2	674	0.581
6.	OX1+NC	PC	0.241	0.112	0.46	14.6	667	0.748

NB: Thickness of fluorescent layer is 150 nm

Table # 1

Effect of increasing of I_{η} with use of primer

Ex. #	Dye concentration Mol/kg	Primer (liquid glass ~80 nm)	Sub- strate type	Absorption				Fluorescence		Fluor. layer thick- ness	
				D ₁	D ₂	D ₂ / D ₁	½	λ _{fluor} , (nm)	Rel. I _n		
1.	OX1+PVA	0.03	-	PC	0.034	0.014	0.41	14.3	668	0.530	150
1.	OX1+PVA	0.03	+	PC	0.035	0.017	0.48	15	674	0.367	150
13.	OX1+PMMA	0.03	+	PC	0.049	0.024	0.49	15,7	665	0.318	200
14.	OX1+PCV	0.03	+	PC	0.017	0.005	0.29	11,8	664	0.991	50

Table # 2

Dependence of I_{fl} level from the polymer substrate nature

Substrate type / Ex. # 1	Absorption				Fluorescence	
	D ₁	D ₂	D ₂ /D ₁	1/2	$\lambda_{\text{fluor,}}$ (nm)	I _{fl.}
Polypropylene	0.024	0.013	0.54	15.0	668	0.177
Polyester	0.015	0.007	0.47	15.7	665	0.206
Polycarbonate	0.031	0.014	0.46	14.3	664	0.425
Polyvinylchlorid e	0.035	0.018	0.45	10.0	660	4.145

NB: Thickness of fluorescent layer is 300 nm

Table # 3

Dependence of I_{η} level from the fluorescent layer thickness on PVC (example # 1)

Substrate type / Ex. # 1	Fluor. layer thick	Absorption			Fluorescence	
		D_1	D_2	D_2 / D_1	$1/2$	$I^{\text{rel.}}_{\eta}$
PC	150	0.034	0.014	0.41	14.3	1.0
PVC	150	0.038	0.016	0.43	10.3	4.0
PVC	300	0.087	0.036	0.41	10.7	22.5
PVC	300	0.074	0.030	0.41	10.0	21.0

Table # 4

Dependence of I_{fl} level from the fluorescent layer thickness on PVC (examples ## 4 and 5)

Ex. #		Dye concentration Mol/kg	Fluor. layer thick- ness (nm)	Sub- strate type	Absorption			Fluorescence		
					D_1	D_2	D_2/D_1	$\lambda_{flour},$ (nm)	λ_{fl}	I_{fl}
4	OX1+NC	$3 \cdot 10^{-2}$	200	PVC	0.044	0.034	0.76	663		4.478
4	OX1+NC	$3 \cdot 10^{-2}$	400	PVC	0.084	0.056	0.63	662		7.145
4	OX1+NC	$3 \cdot 10^{-2}$	500	PVC	0.147	0.081	0.55	661		13.25
5	OX1+NC	$9 \cdot 10^{-2}$	200	PVC	0.177	0.089	0.47	664		5.895
5	OX1+NC	$9 \cdot 10^{-2}$	400	PVC	0.416	0.14	0.38	667		14.7
5	OX1+NC	$9 \cdot 10^{-2}$	500	PVC	0.615	0.240	0.39	669		7.521

Table # 5

Dependence of I_n level from the polymer nature and the fluorescent layer thickness (examples ## 7, 8, 10 and 11)
(examples ## 7, 8, 10 and 11)

Ex. #		Dye concentra- tion Mol/kg	Fluor. layer thick (nm)	Substrate type	Absorption			Fluorescence		
					D_1	D_2	D_2 / D_1	$\lambda_{\text{flour}}, \text{nm}$	$\lambda_{\text{flour}}, \text{nm}$	I_n
10	HIDC+NC	$3 \cdot 10^{-2}$	200	PVC	0.110	0.066	0.06	15.0	673	5.640
10	HIDC+NC	$3 \cdot 10^{-2}$	400	PVC	0.219	0.106	0.48	13.6	674	8.032
7	HIDC+PVA	$3 \cdot 10^{-2}$	300	PC	0.196	0.120	0.61	17.9	665	0.378
11	HIDC+NC	$9 \cdot 10^{-2}$	200	PVC	0.296	0.148	0.50	13.9	674	3.797
11	HIDC+NC	$9 \cdot 10^{-2}$	400	PVC	0.662	0.092	0.44	14.3	678	11.53
8	HIDC+PVA	$9 \cdot 10^{-2}$	100	PC	0.146	0.07	0.50	15.7	672	0.228

Table # 6

Table 1 illustrates the effect of increasing fluorescence intensity by using a filmmaking polymer, which reduces the ability of cationic dyes to form non-fluorescent dimmers and other dyes associates. The table, as well as all the tables given below, utilizes the following designations:

- 5 D_1 - optical density of the monomer form in a maxima of absorption;
- D_2 - optical density of associated forms in a maxima of absorption;
- D_2/D_1 - the ratio, describing the ability of the dyes to form associates;
- $l/2$ - half-width of the absorption band on the 0.7 D_1 level, describing heterogeneity of the absorption band due to the formation of associates and by-products of the specific reaction
- 10 between the dyes and the medium;
- $\lambda\lambda_{\max}$ – maximum of fluorescence;
- I_{η} – intensity of fluorescence in relative figures.

As can be seen from Table 1, the increase of Ox-1 concentration causes I_{η} reduction both in PVA and nitrocellulose, thus increasing of D_2/D_1 and $l/2$. In case of exchanging PVA

15 for the nitrocellulose, the total I_{η} level doubles due to decreased ability of the Ox-1 to form the associates.

Table 2 illustrates the effect of increasing fluorescence intensity by using a primer between the substrate and the active layer, which allows depositing the fluorescent

20 compositions containing solvents, aggressive to the substrate.] Plotting of a liquid silica glass primer 80 nm thick on a PC substrate allows depositing compositions based on PMMA and PVC, containing methylenechloride and dioxane, which also solves the PC substrate.

As can be seen from the Table 2, in the Examples 13 and 14 the fluorescence level

25 increases in 6 and 8 times correspondingly in comparison to the example without the primer (Example 1). Use of primer doubles fluorescence in the Example 1 composition.

Table 3 illustrates the impact of the polymer substrate nature on the fluorescence intensity in the Example 1. The types of substrates are sorted by ascending of fluorescence.

30 As seen, the transition from polypropylene to polyvinylchloride consecutively increases fluorescence, which is maximum for the polyvinylchloride. The consequence for the adhesion of the active layer to the substrate is the same.

The non-cymbate growth of fluorescent signal at increasing the active layer thickness without changing the dye concentration, as shown in the Table 4 with respect to the polymer, testifies that the associated forms of the dye are mostly absorbed on the boundary of the substrate (PCV, in this case) and the active layer. At the same time, the monomeric form of the dye is mostly diluted in the polymeric composition. Due to the same reasons, increasing dye concentration in the active layer bonded on the PVC does not cause depreciation of fluorescence, as in the case of using PC substrate. In some case, we observe even the growth of I_n (compare Tables 5, 6 and 1).

Thus, the proposed ways of increasing fluorescence or the polymeric compositions, containing super-high concentrations of the fluorescent dyes ($3-20 \times 10^{-2}$ Mol/kg of polymer), which usually cause rigid deprecation of fluorescence, can be used for creation of optical recording media for low-cost CD ROM, DVD and WORM discs with simplified structure and with increased quality and stability of data reproduction at reading by fluorescence.

The greatest strengthening of the fluorescent signal is achieved by using primers (2-8 times increase) and polymer substrate, providing effective absorption of the non-fluorescent associates of the dye molecules on its boundary with the active layer (more than 20 times increase).